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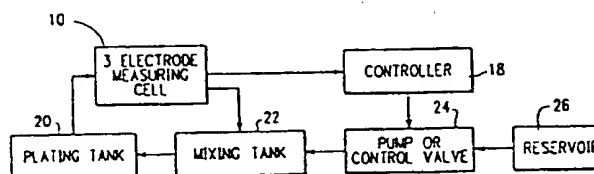
(54) System and method for automatically monitoring and maintaining desired concentrations of metal plating baths.

(57) A system for the automatic, on-line analysis and control of additives in chemical processing solutions in manufacturing processes is disclosed.

The automatic control system embodiment includes a sensing system such as measuring a cell (10) in which appropriate sensors are located. For electrochemical measurements, a three electrode cell with a rotating disk sensor is employed to control agitation of the sample solution. Other sensors on electrodes are used to measure pH and a thermometer is provided to monitor temperature. The sensing process, like the sampling process, is automatically controlled by a controller (18).

The system, in addition to the sensing means and controller, further includes a plating tank (20), a mixing tank (22), a pump or control valve (24) and a reservoir (26). The measuring cell (10) may be disposed in the bath in a standard plating tank in which the plating bath solution is contained. Alternatively, a flow through tank may be used in which the plating solution may flow into and from as desired.

When the sensing means so determines, a replenishment bath from the reservoir can be pumped into the mixing tank by means of the pump or control valve means under the command of signals from the controller which in turn receives output signals from the measuring cell.



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SYSTEM AND METHOD FOR AUTOMATICALLY MONITORING AND  
MAINTAINING DESIRED CONCENTRATIONS OF METAL PLATING BATHS

This invention relates to a system and method for monitoring metal plating bath concentrations, and more particularly to a system or method for electrolytically measuring the concentration of a metal plating bath and automatically replenishing the bath.

U.S. Patent 4,317,705 of Hamada et al for "Method for Measuring Concentration of Oxidant or Reductant" describes the use of a potentiostat in an electrolytic cell to measure the concentration of an oxidant or a reductant. A solid disk platinum or gold electrode is employed as a working electrode located near the counterelectrode and the reference electrode in a capsule through which electrolyte passes. The patent points out the advantages of using a static electrode rather than a rotating disk electrode.

This patent does not discuss organic additives which is one of the primary features of the present invention. Also, the additives employed in the Hamada patent are neither oxidants nor reductants.

U.S. Patent 4,331,699 of Suzuki et al for "Method for Evaluating Electroless Plating" shows in FIG. 1, the use of the coulometric method of measuring an electroless plating bath using a metallic working electrode 2, a reference electrode 8 of Pt, Cu, Ni, Pd, Cr, Rh, Ir or the like, and a counterelectrode 6. A pulse generator produces pulses which test the solution from the electroless plating bath which is in the cell 4. This is relevant in that an electroless plating bath is being measured electrolytically. The patent describes use of copper sulfate and EDTA in the Examples. The Suzuki patent teaches the use of charge pulses applied to the working electrode. The present invention does not apply any charge to the working electrode.

U.S. Patent 4,336,111 of Graunke for a "Method for Determining the Strength of a Metal Processing Solution" describes an in situ method for measuring the strength of an electroless plating solution or an etching solution. This arrangement involves only two electrodes, neither of which rotates.

U.S. Patent 4,350,717 of Araki et al for "Controlling Electroless Plating Bath" describes an automatic system for controlling the composition of the bath by measuring a constituent which is consumed and operating a controller to add the constituent being consumed to the required degree. The concentration of the element in the bath is measured by a spectrophotometer 3 which senses the transmittance at the frequency of the metal complex in the bath which varies as a function of the concentration of the constituent being depleted. The solution is enriched by controlling the valves 22 and 32 in response to the values measured. In a control circuit, a voltage is generated in response to the output of the spectrophotometer and it is compared with a fixed voltage to provide the control signals to the devices being controlled. The present invention does not employ a spectrophotometer. Araki teaches the measurement of a metal complex and not the measurement of any organic additives.

U.S. Patent 4,353,933 is similar to '717 above but it also includes a sensor 4 comprising a specific gravimeter for making measurements of the fluids in the bath. It differs from the present invention in the same ways as the above Araki patent.

#### SUMMARY OF THE INVENTION

An object of the present invention is to provide a system and a method of automatically monitoring and controlling, through replenishment, the concentration level of an additive employed in a metal plating bath by means of an automatic monitor and control system.

Another object of the present invention is to provide a system and method for measuring the presence of the additive in an electroless or electrolytic plating bath by taking a sample of the bath and measuring it in situ.

A further object of the present invention is to provide an automatic system for controlling the concentration of an additive to a plating bath in real time including means for measuring the mixed potential of the bath at zero net current applied to the bath, means for interpreting the mixed potential as a function of the velocity of the bath with respect to the measuring means, and means for refurbishing the bath as a function of the interpreted value.

The invention will now be further described with reference to the accompanying drawings, in which:-

FIG. 1 is a measuring cell used in an embodiment of a system and method for plating according to the present invention.

FIG. 2 is a schematic block diagram illustrating an embodiment of an automatic control system for carrying out a plating bath process and method according to the present invention.

FIG. 3 is a calibration curve for one embodiment of an organic additive which may be used in the present invention.

FIG. 4 is a calibration curve for another embodiment of an organic additive which may be used in the present invention.

FIG. 5 is a calibration curve for a further embodiment of an organic additive which can be employed in the present invention.

FIG. 6 is a calibration curve for still another embodiment of an organic additive useful in the present invention.

FIG. 7 is a calibration curve for the embodiment of FIG. 5 using a different plating bath.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, the schematic drawing illustrates an embodiment of a system for the automatic, on-line analysis and control of chemical processing solutions. Monitoring and control of such solutions in manufacturing processes is particularly critical in order to maintain high standards of quality, throughput and efficiency of plating solutions used in printed circuit board plating and magnetic disk and head plating.

The automatic control system embodiment is shown in the block diagram in FIG. 2 and includes a sensing system such as measuring cell 10 which is illustrated in detail in FIG. 1. The system of FIG. 2 also represents an embodiment for carrying out the process control method of the present invention.

The sensing system 10 consists of one or more sensing cells in which appropriate sensors are located. For electrochemical measurements, a three electrode system 10 as shown in FIG. 1 with a rotating disk sensor 12 is employed to control agitation of the sample solution. Other sensors 30 and 32 on electrodes 14 and 16 are used to measure pH and a thermometer is provided to monitor temperature. The sensing process, like the sampling process, is automatically controlled by the controller. A number of techniques of the sensing subsystem have been successfully performed, including the galvanostatic pulse method, the potentiostatic pulse method, linear sweep methods, the polarization resistance method, the mixed potential method, and a number of spectrophotometric techniques.

The system of FIG. 2, in addition to the sensing means 10, further includes a controller 18, a plating tank 20, a mixing tank 22, a pump or control valve 24 and a reservoir 26. The measuring cell 10 may be

disposed in the bath in a standard plating tank 20 shown in FIG. 1, in which the plating bath solution is contained. Alternatively, a flow through tank may be used as shown in FIG. 1 which the plating solution may flow into and from as desired.

When the sensing means 10 so determines, a replenishment bath from reservoir 26 can be pumped into mixing tank 22 by means of pump or control valve means 24 under the command of signals from controller 18 which in turn receives output signals from the measuring cell 10.

Thus, FIG. 2 illustrates an automatic plating bath replenishment system wherein in situ measurement devices sense the condition of the bath in the plating tank (or in a flow through tank), then feedback such measurements to a controller which in turn controls a pump or valve which introduces replenishment bath as needed for mixing with the sensed bath. The purpose for such system is as follows:

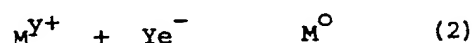
Metal deposits from plating baths which contain organic additives are generally bright and possess properties which are important to the manufacture of multilayer printed circuit boards and multilayer ceramics. The extent to which an organic additive affects the deposition mechanism and hence the properties of the metal film depends on the concentration of the additive in the plating bath. Therefore, in order to maintain precise control over the plating process, it is necessary to accurately monitor the additives and to maintain their concentrations within specified limits. The present invention includes a technique for monitoring the concentration of the organic additive in the bath by observing the mixed potential of the plating system.

This technique utilizes the concept of the mixed potential to determine the organic additive concentration in an electroless plating bath. Organic additives generally participate in the plating process via a surface interaction and as such play a major role in determining the value of the mixed potential. The mixed potential is best defined by considering two or more reactions occurring simultaneously. For

example, in an electroless plating bath, the anodic reaction is the decomposition of the reducing agent.



and the cathodic reaction the reduction of the metal complex



A necessary condition for electroless plating to occur is that the equilibrium potential for the reducing agent,  $E_R^O$ , is more cathodic than the corresponding potential  $E_M^O$ , for the metal deposition reaction. At steady state, the plating rate,  $i_{\text{plating}}$ , is given by:

$$i_{\text{plating}} = i_R = i_M \quad (3)$$

where  $i_R$  and  $i_M$  are the anodic and cathodic partial currents respectively. The potential associated with this steady-state condition is referred to and hereinafter defined as the mixed potential  $E_{MP}$ . The value of the mixed potential lies between  $E_R^O$  and  $E_M^O$  and depends on parameters such as exchange current densities  $i_R^O$  and  $i_M^O$ , Tafel slopes  $b_R$  and  $b_M$ , temperature, etc. Organic addition agents which directly participate in the mechanism for the deposition of the reducing agent or the deposition of the metal, or both, affect these parameters thereby altering the mixed potential. Changes in the value of the mixed potential resulting from different concentrations of a particular organic additive (such as thiodiglycolic acid in the Ni/B bath) can then be used to monitor the concentration of the organic additive in the electroless plating bath. This is illustrated in the examples which follow.

## EXAMPLE 1

Initial measurements were performed in a proprietary nickel-boron bath. A rotating disk system was employed wherein the substrate to be plated was centrally positioned in a plastic jacket or cylinder. The substrate was composed of pure nickel while the reference electrode was a saturated calomel electrode immersed in the electroless plating bath. Calibration curves obtained as a function of rotation rate for thiodiglycolic acid are illustrated in FIG. 3. The critical concentration range lies between 50 and 150 ppm. It can be seen from FIG. 3 that this technique is highly sensitive to the concentration of thiodiglycolic acid in this concentration range.

## EXAMPLE 2

Measurements of the mixed potential were also performed with thiodipropionic acid in the plating bath. This data is shown in FIG. 4 as a function of rotating rate. It can be seen that while the rotation rate dependence is different in the case of thiodipropionic acid compared to thiodiglycolic acid, the technique is once again very sensitive to the concentrations of this additive in the plating bath.

Further investigations have revealed that the additive monitoring technique described in this disclosure can also be used to monitor organic additives in other electroless and electrolytic plating baths. Details are given in the examples which follow.

## EXAMPLE 3: Additive monitoring in electrolytic copper plating baths.

An organic brightening agent used commonly in copper plating baths is thiourea,  $\text{H}_2\text{NCSNH}_2$ . The mixed potential technique was applied to an electrolytic copper bath containing this additive. The complete composition of the plating bath was as follows:



$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	10	g/l	
EDTA	14.9	g/l	$T=50^\circ\text{C}$

The calibration curve obtained for thiourea obtained in this plating bath is shown in FIG. 5.

EXAMPLE 4: 2-Benzothiazolethiol monitoring in copper plating baths.

2-Benzothiazolethiol is often a preferred organic additive in both electrolytic and electroless copper plating baths. The technique described in this disclosure was applied to monitor 2-benzothiazolethiol in such a bath. The calibration curve obtained is displayed in FIG. 6. The plating bath had the following composition:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	10	g/l	
EDTA	44.7	g/l	
$\text{H}_2\text{CO}$	3.5	ml/l	$T=72^\circ\text{C}$

EXAMPLE 5: Additive monitoring in electroless copper baths.

Electroless copper baths frequently contain thiourea as a brightener. The concentration of the brightener drifts unpredictably as it gets incorporated into the film or undergoes chemical reactions. In order to monitor the concentration of thiourea in electroless plating baths, the mixed potential technique was applied to the bath with the following composition:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	10	g/l	
EDTA	14.9	g/l	
$\text{H}_2\text{CO}$	3.0	ml/l	$T=50^\circ\text{C}$

The calibration curve given in FIG. 7 shows that this technique is very sensitive to the concentration of thiourea.

What has been described is a novel system and apparatus for monitoring and controlling the concentrations of additives in a plating bath both

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in situ and in real time. The apparatus may be employed in the monitoring and controlling of other chemical processes as well. Likewise, one skilled in the art will appreciate that the process method described herein can also be utilized in other chemical processes.

CLAIMS

1. A system for plating materials of the type including a first vessel containing a plating bath initially having a desired concentration of an organic additive and a second vessel containing a supply of said organic additive for said plating bath, said system being characterised by comprising an arrangement for automatically controlling the concentration of said additive in said plating bath comprising:

means for obtaining an electrical measurement of said plating bath wherein said electrical measurement is a parameter dependent on the concentration of said additive in said bath,

means for detecting changes in said electrical measurement indicative of changes in said additive concentration in said bath,

means responsive to said detecting means for providing a control signal representative of said changes in additive concentration in said bath, and

means connected between said first and second vessels for introducing a selected amount of said organic additive from said second vessel into said first vessel in accordance with said control signal to maintain said desired concentration of said additive in said plating bath.

2. A system for plating materials according to Claim 1, in which said means for obtaining an electrical measurement includes

means for measuring the mixed potential  $E_{MP}$  (as hereinbefore defined) of said plating bath wherein said mixed potential is a parameter dependent on the concentration of said additive in said bath, and said detecting means includes

means for detecting changes in said mixed potential indicative of changes in said additive concentration in said bath.

3. A system for plating materials according to Claim 2, said measuring means being applied directly in situ to said plating bath in said first vessel, and wherein said measuring means includes an electrode system having a rotating disc sensor and reference electrodes for performing an electrolytic measurement of the mixed potential  $E_{MP}$  of said bath.
4. A system for plating materials according to Claim 2, further including a by-pass tank connected to said first vessel for obtaining a sample of said plating bath in said first vessel, and wherein said measuring means is applied to said sample of plating bath in said by-pass tank and includes an electronic system having a rotating disc sensor and reference electrodes for performing an electrolytic measurement of the mixed potential  $E_{MP}$  of said bath.
5. A system for plating material according to Claim 2, 3 or 4, in which said detecting means including an electronic data processing means having calibration data relating plating concentration to said electrolytic measurement for producing an output signal specifying additives value for measured concentrations.
6. A system for plating materials according to Claim 5, in which said means responsive to said detecting means includes a pump and valve combination disposed between said first and second vessels responsive to said output signal from said electronic data processing means from transferring an amount of said additive from said second vessel to said

first vessel to maintain said desired concentration of said additive in said plating bath.

7. A system for plating materials according to Claim 6, in which said rotating disc sensor and said electrode system measuring the mixed potential of said plating bath with a zero net current applied to said bath, and

said electronic data processing detecting means interpreting said mixed potential measurement as a function of the relative velocity of said plating bath and said rotating sensor.

8. A system for plating materials according to Claim 7, said electronic data processing detecting means having stored therein data associated with plating bath concentration values measured as a function of rotation velocities of said rotating disc sensor.

9. A system for plating materials according to Claim 8, said additive in said plating bath and said second vessel being thiourea.

10. A system for plating materials according to Claim 8, said additive in said plating bath and said second vessel being 2-benzothiazolethiol.

11. A method for controlling the concentration of an organic additive in a system for plating materials of the type including a first vessel containing a plating bath having a desired concentration of an organic additive and a second vessel containing a supply of said organic additive for said plating bath, comprising the steps of:

electrically measuring the mixed potential  $E_{MP}$  (as hereinbefore defined) of said plating bath wherein said mixed potential is a parameter dependent on the concentration of said additive in said bath,

detecting and analyzing changes in said mixed potential for determining changes in said additive concentration in said bath, and

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automatically adding a selected amount of said organic additive from said second vessel into said first vessel in accordance with said determined changes in said additive concentration to maintain said desired concentration of said additive in said plating bath.

12. A method for controlling the concentrations of a plating bath according to Claim 11, wherein said electrical measuring step is applied directly in situ to said plating bath in said first vessel, and wherein said electrical measurement step includes performing an electrolytic measurement of the mixed potential  $E_{MP}$  of said bath.

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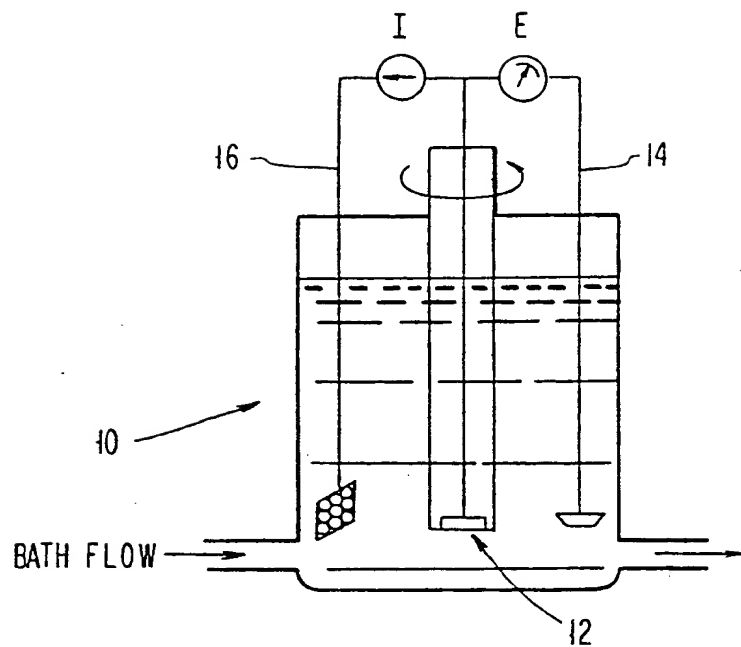


FIG. 1

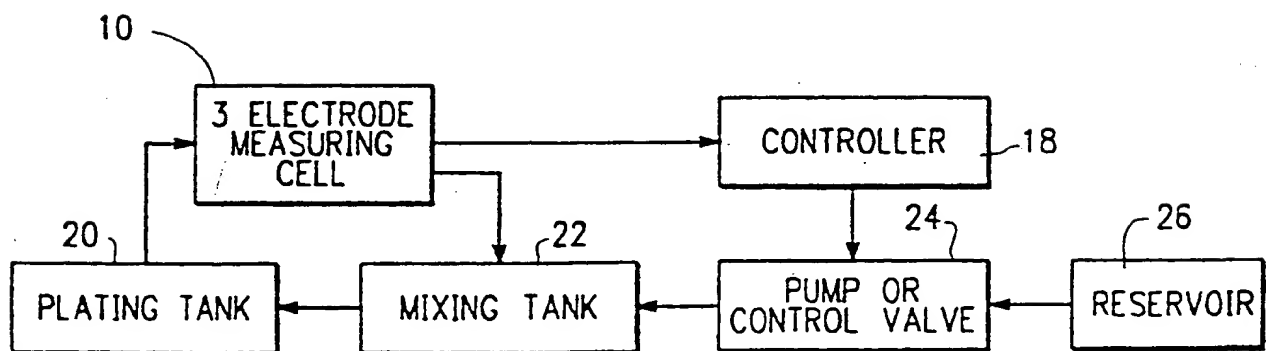
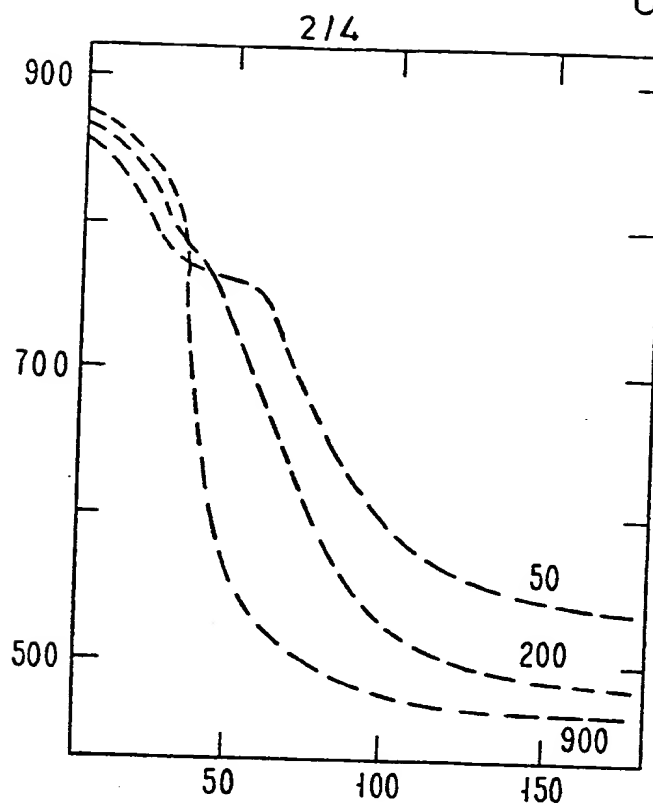


FIG. 2

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**FIG. 3**  
POTENTIAL  
(mV) vs. SCE



**FIG. 4**  
POTENTIAL  
(mV) vs. SCE

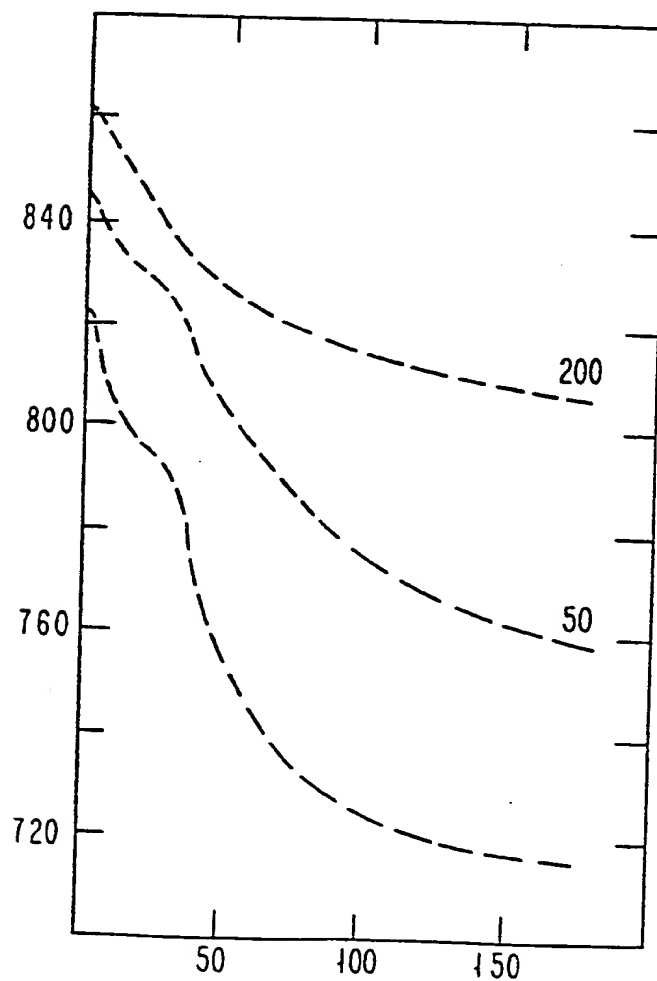




FIG. 6

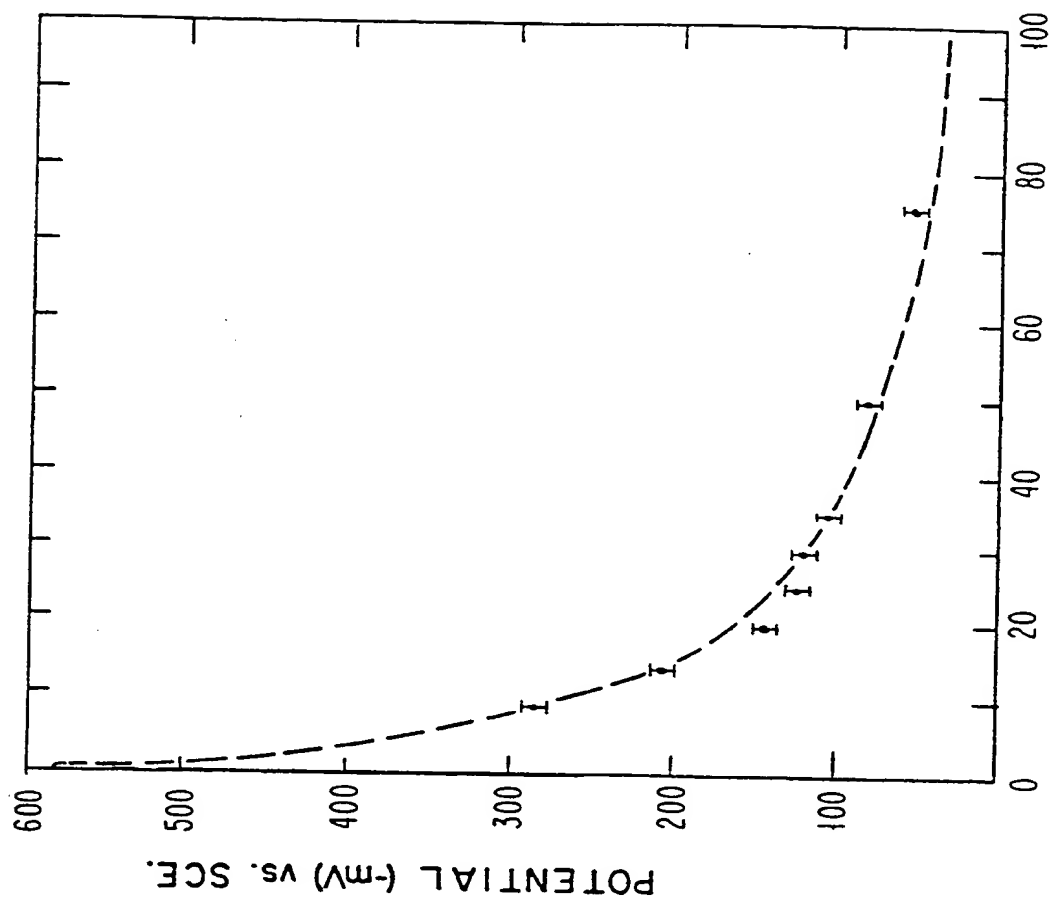
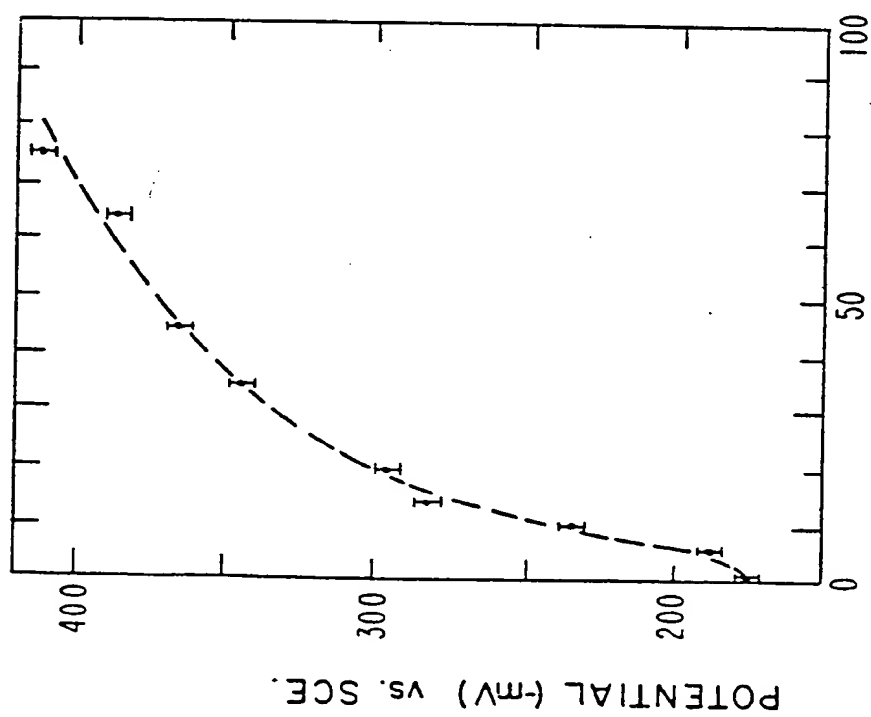


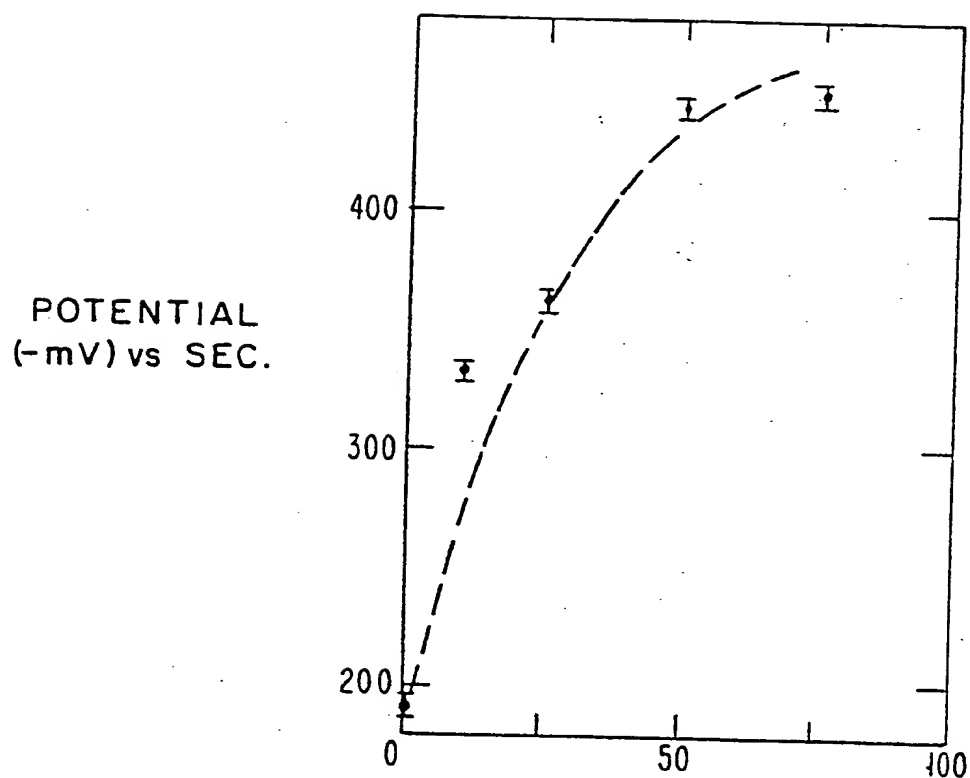
FIG. 5



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FIG. 7



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54 System and method for automatically monitoring and maintaining desired concentrations of metal plating baths.

57 A system for the automatic, on-line analysis and control of additives in chemical processing solutions in manufacturing processes is disclosed.

The automatic control system embodiment includes a sensing system such as measuring a cell (10) in which appropriate sensors are located. For electrochemical measurements, a three electrode cell with a rotating disk sensor is employed to control agitation of the sample solution. Other sensors on electrodes are used to measure pH and a thermometer is provided to monitor temperature. The sensing process, like the sampling process, is automatically controlled by a controller (18).

The system, in addition to the sensing means and controller, further includes a plating tank (20), a mixing tank (22), a pump or control valve (24) and a reservoir (26). The measuring cell (10) may be disposed in the bath in a standard plating tank in which the plating bath solution is contained. Alternatively, a flow through tank may be used which the plating solution may flow into and from as desired.

When the sensing means so determines, a replenishment

bath from the reservoir can be pumped into the mixing tank by means of the pump or control valve means under the command of signals from the controller which in turn receives output signals from the measuring cell.

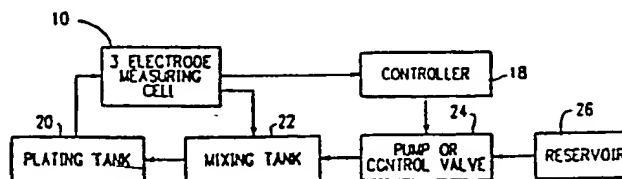


FIG. 2



European Patent  
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# EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	JOURNAL OF ELECTROCHEMICAL SOCIETY, vol. 127, no. 2, February 1980, pages 365-369; M. PAUNOVIC "An electrochemical control system for electroless copper bath" * page 366, column 1, paragraph 4; column 2, paragraph 5 - page 367, column 2, paragraph 1 *	1,2,11	G 01 N 27/56 G 01 N 27/46 G 01 N 27/42 G 01 D 21/02 C 23 C 18/16 C 25 D 21/12
Y	FR-B-2 371 522 (KOLLMORGEN TECHNOLOGIES CORP.) * claims 1, 12-17; page 1, paragraphs 1, 3; page 3, lines 10-18, 32-37; page 5, lines 10-15; page 7, line 32 - page 8, line 35; page 9, line 11 - page 10, lines 6, 36 - page 11, line 24; page 18, line 28 - page 19, line 5 *	1,2,11	
A	* whole document *	3-10, 12	TECHNICAL FIELDS SEARCHED (Int. Cl. 4) G 01 N 27/00 C 23 C 18/00 G 05 D 21/00
A	DE-A-2 911 073 (SIEMENS AG) * claims; page 5, lines 23-35; page 8, line 16 - page 10, line 23 *	1,11	
A	US-A-4 406 249 (K. ARAKI et al.) * whole document *	1,11	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 17-10-1986	Examiner VINSOME R M
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	